

Effects of Nitrogen Implantation on Oxide Growth and Quality

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Abstract—The effects of implanting nitrogen prior to gate oxidation are presented. Three different doses of N^+ , N_2^+ , and Si^+ were implanted, followed by a 20-minute 950°C dry oxide growth. Growth rate, interface quality and breakdown strength were measured. Results show up to a 70% reduction in growth rate for high dose nitrogen implants, but no change for silicon implants. The interface trap density decreased with increasing dose for all three species. Oxides grown over N_2^+ implanted silicon showed field strengths comparable to standard oxides.

1. INTRODUCTION

The gate oxide is critical to MOSFET performance. Modern devices demand an ultrathin ($< 3\text{nm}$) oxide with low fixed charge and interface trap densities, hot carrier and boron diffusion resistance, and high breakdown strength. As device dimensions and the gate oxide thickness are scaled down, it becomes increasingly difficult to grow high quality oxides that meet these performance criteria.

For several years, it has been known that incorporating nitrogen into the gate oxide can produce beneficial effects, namely improved resistance to boron diffusion and hot electrons [1]. Traditionally, nitridation has been done using N_2O , NO , or NH_3 ambients during or after oxide growth [2]. However, these methods suffer several shortfalls. With NH_3 , the excess hydrogen can create trap sites [3]. For this reason, N_2O and NO are usually used. But the incorporation rate for these two gases depends highly on the temperature and the flow rate [4], leading to process variation. Furthermore, the amount of nitrogen that can be incorporated with N_2O and NO is relatively low [2]. Nitrogen implantation prior to oxidation has been suggested as an alternative method of nitridation [5]. Because the nitrogen is implanted, the dose can be precisely controlled, and much higher doses can be achieved. In addition, oxides grown over nitrogen implanted silicon exhibit much lower growth rates [5-10]. The decreased rate is beneficial because it allows for longer oxidation times, improving process control, and higher temperatures, increasing quality. One study of oxides grown after nitrogen implantation shows an

improvement in breakdown strength for medium nitrogen doses [9]. In addition, nitrogen can be selectively implanted into devices to enable a multiple gate CMOS process [10]. Areas implanted with nitrogen will have thinner oxides than those that don't, giving rise to different threshold voltages. Novel designs that could not be made previously can be fabricated using this approach.

The intent of this experiment was to explore the effects of implanted nitrogen on the oxide growth rate and quality. Three implanted species were examined: N^+ (amu 14), N_2^+ (amu 28), and Si^+ (amu 28). The silicon implant was done to determine if implant damage causes the reduced oxidation rate. Since it has a similar atomic mass to N_2 , it should produce a similar damage profile. A SemiTest SCA-2500 was used extensively to study the interface quality. It has the ability to measure interface trap density, surface substrate doping, minority carrier lifetime, fixed oxide charge and flatband charge through the use of what is essentially an electro-optical C-V measurement.

2. EXPERIMENTAL

Nine p-type $<100>$ 10 ohm-cm wafers were used. An 85nm screening oxide was grown prior to implant. Surface charge analysis was done using a SemiTest SCA-2500 to obtain a baseline. Photoresist was coated on the wafers and then the resist on half of each wafer was exposed and developed away. This protected one side of the wafer from implant. By implanting only one half of the wafer, direct correlations could be made between the implanted and non-implanted sides.

SRIM simulation software was used to determine appropriate ion energies for each species. The implant was targeted so that the peak would occur at the oxide interface, for a maximal effect. It was assumed that N_2^+ behaves similarly to Si^+ , since SRIM can only simulate monatomic species. Table 1 lists the doses and energies used. Note that the N^+ dose was twice that of the N_2^+ so that the same amount of nitrogen was incorporated.

After implantation, the resist was stripped with hot Nanostrip and an RCA clean was done. The highest dose Si^+ wafer was accidentally broken in this step, which left it unsuitable for measurement with the SCA. The screening

oxide was stripped with buffered HF, followed by an RCA clean.

To ensure a good interface, special care was taken during the cleans. The clean tanks were rinsed thoroughly with DI water, then a diluted HCL mixture was poured into the tanks to remove metallic contaminants. The HCL mixture was allowed to sit in the tanks for about 20 minutes then the tanks were rinsed again. Fresh P-Lo chemicals from Ashland Chemical were mixed for the APM and HPM baths. The ratio for the APM bath was 16:3:1 H₂O:H₂O₂:NH₄OH. The HPM bath was mixed 16:3:1 H₂O:H₂O₂:HCl. The temperature for both baths was kept at a fairly low 65-70°C to minimize surface roughening. Particle counts were taken with a Tencor Surfscan before and after cleans to monitor their effectiveness.

Immediately prior to oxidation, a TCA clean was done on the furnace tube and quartz wafer boat at 1050°C for 15 minutes. This helped remove any possible metallic contaminants. A 20-minute nitrogen purge was done after the clean to flush the chlorine from the system.

A 20-minute, 950°C dry oxidation followed by a 20-minute argon anneal at 950°C was performed on the nine half-implanted wafers. The wafers were pushed and pulled at 700°C to limit atmospheric oxide growth. The oxide thickness was measured using an ellipsometer, and the SCA was used to make 37-point maps of the wafers. Maps for the doping concentration, defect density, flat band charge, and carrier lifetimes were obtained.

Aluminum was evaporated onto the medium and high dose nitrogen implanted wafers to make capacitors for breakdown strength characterization. However, aluminum adhesion problems were encountered, so the aluminum was stripped and the wafers were recleaned. The HF dip step in the RCA clean was eliminated to preserve the oxide thickness. To drive the water from the oxide, the wafers were annealed in argon for 1 hour at 900°C. The oxide thickness was remeasured and new SCA maps were made. It was found that the wafers lost approximately 10-15Å of oxide after this processing. This left the wafer with the highest dose of N⁺ with an oxide deemed too thin (<3.5nm) to perform breakdown tests on.

To make the capacitors, aluminum was sputtered on the highest dose N₂⁺ wafers and medium dose N⁺ wafer using the CVC-601 sputterer. Shadow masks with 37, 35mm holes were used to pattern the aluminum. To help prevent plasma damage to the oxide, a low power 500W sputter was done for 5 minutes, followed by a 40 minute sputter at 1000W. After sputtering it was observed that the shadow masks had shifted during the run, producing small streaks of aluminum instead of perfect circles. This effect was especially bad on the medium dose N⁺ wafer, so it was removed from breakdown strength testing.

The sputtered capacitors were covered with resist so the backside oxide could be etched. Buffered oxide etch was used. To ensure a good backside contact, aluminum

was sputtered on the backs of the wafers at 2000W for 20 minutes. The wafers were then sintered at 410°C for 20 minutes in forming gas (H₂/N₂).

Dielectric breakdown strength was measured on the medium and high dose N₂⁺ wafers using a Hewlett Packard 4145B Semiconductor Parameter Analyzer. This test was performed by sweeping a voltage across the oxide and measuring the current; a vertical jump in the current indicated a breakdown. A current limiting resistor was placed in series with the MOS capacitor. This resistor, along with the other resistances in the circuit, created an IR curve that could be superimposed over the breakdown curve. The breakdown voltage was measured by measuring the voltage difference between the IR curve and the point of breakdown.

Table 1: Doses and energies used for each ion species

| Species | Doses (ions/cm ²) | Energy (keV) |
|-----------------------------|-------------------------------|--------------|
| N ⁺ | 2E14, 8E14, 2E15 | 32 |
| N ₂ ⁺ | 1E14, 4E14, 1E15 | 58 |
| Si ⁺ | 1E14, 4E14, 1E15 | 58 |

2. RESULTS AND DISCUSSION

A. Oxidation

Figure 1 shows the oxide thickness plotted versus dose for each species. Note that the nitrogen dose is plotted as the actual number of atoms incorporated, rather than implant dose. This graph shows that the oxidation rate decreased substantially with the higher doses of nitrogen. The N⁺ implant caused the largest effect, resulting in a 70% decrease in growth rate. The silicon implant had virtually no effect, which means that the decrease in growth rate is not due to implant damage. It is not known why there are differences between the N⁺ and N₂⁺ implants. It is possible that the implant peaks were shifted away from the oxide interface. Additional studies, such as SIMS analysis, need to be conducted to determine the implant profiles.

These results compare favorably to previously published reports [5-10], however, oxide growth rates vary widely. Liu et al. [6], Lopez [7] and Wescott [8] observed larger reductions in growth rate with smaller doses. The results obtained in this experiment most closely match those of Kurinec et al. [9] and Soleimani et al. [5]. The Soleimani group did a deep N₂⁺ implant (0.1µm) followed by an anneal to pile-up the nitrogen at the screening oxide interface. The screening oxide was then stripped and the gate oxide was grown. The reported growth rates appear to be related to the initial implant profile. Again, more analysis needs to be conducted to determine how the profile affects growth rate.

B. Interface Quality

The 37-point SCA wafer maps were used to analyze the changes in interface quality. Because the wafers were only half implanted, direct differences could be observed on some of the wafers. Figure 2 shows the change in interface trap densities (D_{it}) versus dose. As shown, all three species produced a change, with D_{it} generally trending downward with increasing dose. Surprisingly, the silicon implant had the largest effect, followed by the N_2^+ . The effect of the N^+ was relatively small. The implants appear to be passivating the surface states. The passivating effects of nitrogen have been observed in N_2O growth [11]; however, it is unknown why the silicon appears to be doing the same. It is possible that implant damage is a factor.

Figure 3 shows the change in surface substrate doping (N_{sc}) versus dose. The initial substrate doping for all wafers was approximately $4E14\text{ cm}^{-3}$. All three species caused a decrease substrate doping with increased dose. Again, the silicon showed the strongest effect followed by the N_2^+ and the N^+ . It is likely that the substrate doping is not changing this substantially, but some other effect is causing the SCA to report it as such.

C. Dielectric Strength

Figures 4 and 5 show cumulative percentage plots of the breakdown strength of oxides grown over the medium and high dose N_2^+ implants versus oxides grown over the non-implanted silicon. The nitrided oxides showed breakdown strengths similar to the standard oxides. However, the nitrided oxides were thinner. It is speculated that if similar thicknesses were compared, the nitrided oxides would show higher breakdown strength. Kurinec et al. [12] found significant improvements in dielectric strength in 12nm oxides for medium doses ($5E14\text{ ions/cm}^2$) of N^+ . Doses at and above $1E15\text{ ions/cm}^2$ showed poor dielectric strength, possibly due to heavy implant damage.

A large percentage of the tested capacitors were shorts. This is probably due to the large area of the aluminum streaks used for capacitors. Thus, there was a high probability of a defect being present in the oxide. Further studies need to be done with smaller capacitor areas.

3. CONCLUSIONS

Nitrogen implantation can be beneficial when growing thin oxides. N^+ or N_2^+ doses in the range of $4E14$ to $2E15$ have been shown to significantly reduce the oxidation rate, which can improve process control. Furthermore, results indicate some improvements to oxide quality as well, with reductions in interface trap density observed in implant

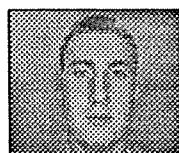
doses above $1E15\text{ ions/cm}^2$. Dielectric strength is at a minimum consistent with standard oxides.

4. REFERENCES

- [1] E. P. Gusev, H.-C. Lu, E. L. Garfunkel, et al., *IBM J. Res. and Develop.*, vol. 43, no. 3, p. 265, 1999.
- [2] E. P. Gusev, H.-C. Lu, E. L. Garfunkel, et al., *IBM J. Res. and Develop.*, vol. 43, no. 3, p. 266, 1999.
- [3] S. K. Kurinec, M. A. Jackson, K. C. Capasso et al., *Mat. Res. Soc. Symp. Proc.*, vol. 567, p. 265, 1999.
- [4] K. A. Ellis and R. A. Buhrman, *IBM J. Res. and Develop.*, vol. 43, no. 3, p. 288, 1999.
- [5] H. R. Soleimani, B. S. Doyle, and A. Philipossian, *J. Electrochem. Soc.*, vol. 142, no. 8, p. L132, 1995.
- [6] C. T. Liu, Y. Ma, J. Becerro, et al., *IEEE Electron Dev. Lett.*, vol. 18, no. 3, p. 105, 1997.
- [7] L. Lopez, *J. Microelectronic Res.*, vol. 15, p. 24, 1997.
- [8] N. Wescott, *J. Microelectronic Res.*, vol. 17, p. 18, 1999.
- [9] S. K. Kurinec, M. A. Jackson, K. C. Capasso et al., *Mat. Res. Soc. Symp. Proc.*, vol. 567, p. 266, 1999.
- [10] B. Doyle, H. R. Soleimani, and A. Philipossian, *IEEE Electron Dev. Lett.*, vol. 16, no. 7, p. 301, 1995.
- [11] N. Gonan, A. Gangnaire, D. Barbier, et al., *J. Appl. Phys.*, vol. 76, p. 524, Nov. 1994.
- [12] S. K. Kurinec, M. A. Jackson, K. C. Capasso et al., *Mat. Res. Soc. Symp. Proc.*, vol. 567, p. 267, 1999.

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Figure 1: Oxide thickness vs. Dose*

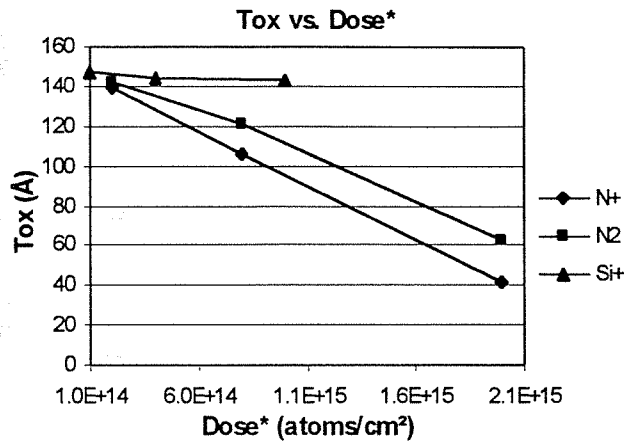


Figure 2: Interface trap density vs. Dose*

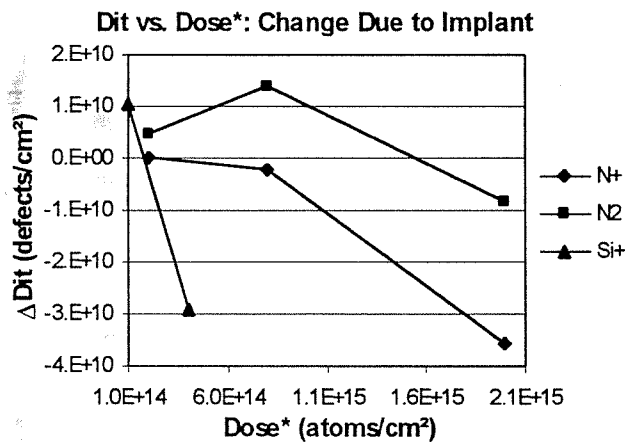


Figure 3: Surface substrate doping vs. Dose*

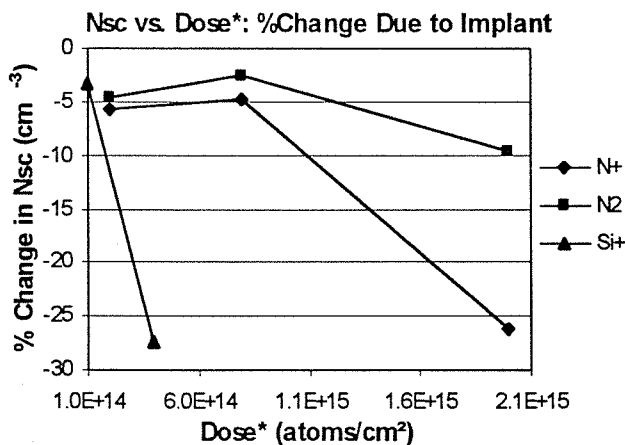


Figure 4: Dielectric breakdown strength of medium dose nitrided oxide vs. non-implanted oxide

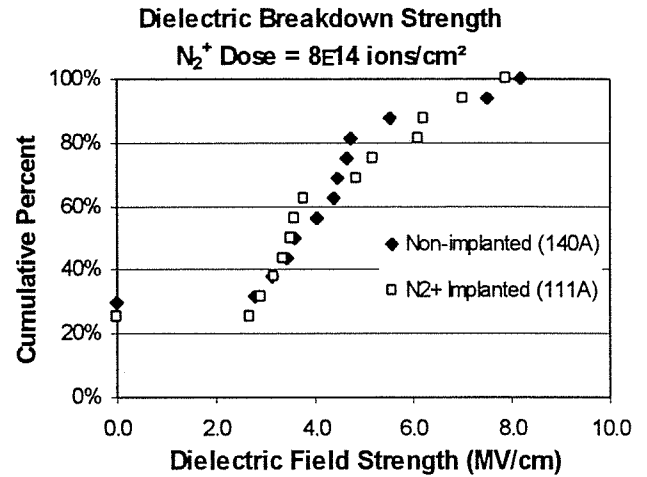
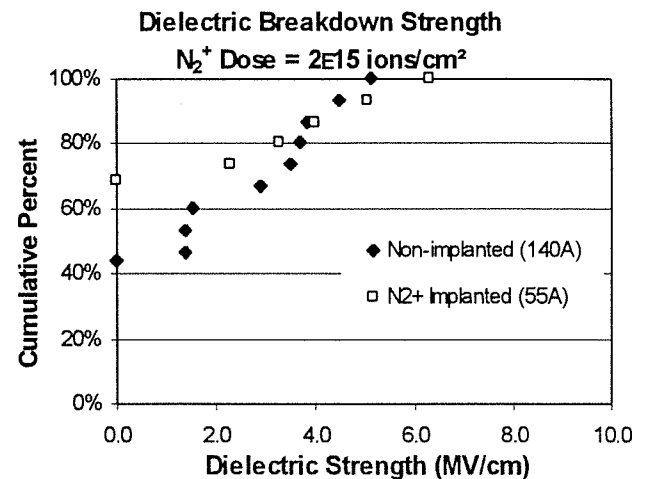


Figure 5: Dielectric breakdown strength of high dose nitrided oxide vs. non-implanted oxide



* Dose is reported as a function of the actual number of atoms incorporated, instead of the implant dose.